

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Fluidised Hydroforming

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the Laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved fluidised catalytic hydroforming processes for converting hydrocarbon fractions boiling within the motor fuel boiling range from 15 low knock rating fuels into high octane number motor fuels.

Hydroforming is a well known and widely used process for treating hydrocarbon fractions boiling within the motor fuel or naphtha range to upgrade the same or increase the aromaticity and improve the anti-knock characteristics of said fractions. By hydroforming is ordinarily meant an operation conducted at elevated temperatures and pressures in the presence of solid catalyst particles and hydrogen whereby the hydrocarbon fraction is increased in aromaticity and in which operation there is no net consumption of hydrogen. Hydroforming operations are usually carried out in the presence of hydrogen at temperatures of 750°-1150°F. in the pressure range of about 50-1000 lbs. per sq. inch and in contact with such catalyst as molybdenum oxide or chromium oxide, or, in general, oxides and sulfides of metals of Groups IV, V, VI, VII, and VIII of the periodic system of elements, alone, or generally supported on a base or spacing agent such as alumina gel, precipitated alumina or zinc aluminate spinel. Aromatisation is carried out in the presence or absence of hydrogen in the presence of the same general class of catalysts at temperatures of about 750°-1150°F., but at pressures of from atmospheric to at most

about 100 lbs. per sq. inch.

It has previously been proposed to effect the hydroforming of naphtha fractions in a fluidised solids reactor system in which naphtha vapors are passed continuously through a dense, fluidised bed of hydroforming catalyst particles in a reaction zone, spent catalyst being continuously withdrawn from the dense bed and passed to a separate regeneration zone where inactivating carbonaceous deposits are removed whereupon the regenerated catalyst particles are returned to the main reactor vessel. Operation of previous processes has been limited to low catalyst to oil ratios (around 1:1) by selectivity considerations since higher ratios resulted in excessive carbon formation. Moreover, high regeneration temperatures have not been possible due to steam deactivation of the catalyst. These factors limit the transfer of heat from the regenerator to the reactor via the catalyst and make it necessary to provide cooling coils in the regenerator and to provide furnaces or other means for supplying heat to the reactor either directly or indirectly through preheating the reactants and/or the hydrogen-rich recycle gas. It is now proposed to overcome some of these shortcomings particularly as to heat balance between the reactor and regenerator by circulating a stream of inert solids in addition to the circulating catalyst stream in a manner hereinafter described. In this way, heat released in the regenerator can be transferred as sensible heat of the inert solids to the reactor thereby obviating or minimising the necessity for supplying heat of reaction through catalyst circulation and/or preheat of the feed and recycle gas. Under these circumstances, the catalyst circulation rate can be independently controlled to any desired low value and high temperature preheating of the recycle gas and naphtha feed streams is unnecessary.

Thus the present invention relates to a 90

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process whereby hydrocarbon fractions boiling within the motor fuel range may be hydroformed in an advantageous manner by the fluidised solids technique in which substantial quantities of inert solids are circulated in addition to the circulating catalyst stream, and further relates to a process whereby hydrocarbon fractions boiling within the motor fuel range may be hydroformed in a fluidised solids reactor system in which heat released in the regeneration of the catalyst particles may be readily transferred from the regeneration vessel to the reaction vessel, and whereby hydrocarbon fractions boiling within the motor fuel range may be hydroformed by the fluidised solids technique with low catalyst to oil ratios but at high temperatures and without excessive preheating of the naphtha feed and without the circulation of excessive amounts of recycle gas and without heating the recycle gas to excessively high temperatures.

The present invention particularly relates to a simple, effective method for providing an inverse temperature gradient as hereinafter defined, in a fluidised solids reactor vessel, and to provide a simple, effective method for providing an inverse temperature gradient in a fluidised solids reactor vessel while still maintaining essentially concurrent flow of catalyst and oil through the reactor.

It has now been found that the hydroforming or aromatisation of petroleum fractions boiling within the motor fuel boiling range in a fluidised solids reactor system can be carried out to greater advantage if extraneous heat-carrying or heat transfer solids are circulated between the reactor vessel and the regeneration vessel in a particular manner, as hereinafter described. It is, of course, known to use so-called pebble heaters to heat up an extraneous heat-carrying solid for circulation through a reaction zone in order to convey some or all of the heat required for carrying out the desired reaction or operation into the reaction zone. In practising the present invention, however, a circulating stream of inert fluidised solids is provided to carry the necessary heat from the regenerator to the reactor, thus making it possible to operate with as low a circulation rate of catalyst as desired, thus reducing carbon formation, and also oxygen as well as hydrogen requirements. The hot inert solids stream is discharged into the top of the reactor dense bed, which may be provided with baffles or perforated plates with downcomers or other devices to prevent top-to-bottom mixing of the catalyst and thereby maintain the inverse temperature gradient. The relative rates of circulation of catalyst and inert heat transfer solids are controlled by separate slide valves on individual standpipes through which the two solids streams are withdrawn from the reactor and the regenera-

tor. The stream of inert solids is discharged from the reactor into the stream of regeneration air for transport to the regenerator upstream of the point of addition of the spent catalyst, so that the heat absorptive capacity of the inert solids will preclude overheating the catalyst which may occur through combustion of the carbonaceous deposits thereon during its travel through the transfer line into the regenerator vessel. Extraneous heat may be added, if desired, to the circulating solids stream by introducing a combustible oil or gas directly into the regenerator. The regenerated catalyst particles in admixture with a small amount of inert heat transfer solids are discharged from the regenerator via a standpipe, or the like, into a stream of recycle gas which carries the mixture back to the reactor. Because of the great flexibility possible in the amount of heat provided by the circulating inert solids, it is not necessary to preheat the feed to temperatures that might result in thermal degradation of the feed. In fact, it is possible to eliminate entirely the feed preheat furnace and to heat the feed stream only to the temperatures possible by heat exchange with product streams. Further, it is not necessary to circulate such large volumes of recycle gas and it is not necessary to heat the recycle gas to the high temperatures of about 1200°F. that are normally required. This eliminates or minimises the possibility of coking in the recycle gas fired coil. Moreover, it is possible with this arrangement to operate with recycle gas temperatures of 1000°F. or less, which permits using carbon steel furnace tubes in place of the more expensive alloy tubes required for the high recycle gas temperatures previously necessary. By introducing the hot inert solids stream into the top of the dense reactor bed, an inverse temperature gradient, i.e., a gradient whereby the upper zones of the reactor are at a higher temperature than the lower zones, is established whereby the reaction mixture contacts catalyst in a final conversion stage or zone where the temperature is somewhat above the average for the entire reaction zone.

The present invention therefore comprises a process for hydroforming hydrocarbons, boiling in the motor fuel boiling range comprising contacting the said hydrocarbons in a reaction zone, and under hydroforming conditions, with a dense, fluidised bed of hydroforming catalyst particles, and continuously introducing into the top of the said reaction zone a stream of hot, inert, solid particles which are maintained in a fluidised state therein, whereby the upper parts of the said reaction zone are maintained at a higher temperature than the lower parts thereof, removing spent catalyst particles from the said reaction zone and also removing the said inert, solid particles from the bottom

of the said reaction zone, mixing the removed inert solid particles with the removed spent catalyst particles and transferring the mixture thus obtained to a regeneration zone, wherein the spent catalyst particles are regenerated, and the inert solid particles are heated by the heat of regeneration of the catalyst particles, removing regenerated catalyst particles and recycling them to the said reaction zone, and removing hot inert solid particles and recycling them to the top of the said reaction zone.

Reference is made to the accompanying drawing illustrating a diagrammatic flow plan of the process in accordance with the present invention.

In the drawing, 10 is the reactor vessel and 40 is the regenerator vessel in the fluidised solids reactor system. Fresh feed or charging stock, which may be a virgin naphtha, cracked naphtha or Fischer-Tropsch naphtha having a boiling range of from about 130°-430°F., is supplied under pressure and preheated to a desired temperature through line 12 to suitable distributor nozzles 13 in the lower portion of the reactor vessel 10. Catalyst mixed with a small amount of inert heat transfer solids is supplied to the reactor vessel 10 in finely divided condition in suspension in a hydrogen-containing gas, preferably recycle hydrogen-rich process gas through inlet line 14 which discharges into inlet cone 15 in the lower portion of the reactor vessel. Solid particles and carrying gas are discharged from the inlet cone through a perforated plate or grid 16 which serves to distribute the incoming material uniformly over the entire cross-section of the reactor vessel. A stream of hot inert solids containing a small amount of catalyst particles is discharged through line 60 against baffle 62 into the upper part of the reactor vessel 10 from where the solid particles drop into the upper part of the reactor dense bed. Means such as one or more perforated grids 63 or plates and downcomers are preferably provided to prevent rapid dispersal of the solids supplied to the top of the bed down into the main fluidised body of catalyst in the reactor.

The inert, heat transfer solids are preferably coarser and/or of greater density than the catalyst used in the process. Typical solids which may be used are metal spheres or ceramic balls or granules preferably of corundum or gamma alumina or fused silica. It is necessary that these materials have no adverse effects upon the catalytic reactions occurring in the reactor and that they be stable or resistant to breakdown due to the temperature and mechanical action to which they are subjected. Unless the inert heat transfer solids are relatively heavy or have a bulk density at least 1.5 times the bulk density of the catalyst, they should be no

smaller than about 100 microns diameter and should preferably be in the range of 125-300 microns diameter.

The feed or charging stock vapors introduced via nozzles 13 and the hydrogen-containing gas supplied through inlet chamber 15 and distributor grid 16 pass through the reaction zone at a superficial velocity of about 0.2 to 0.9 ft. per second at reactor conditions depending upon the pressure. For example, the velocity should be below 0.6 ft. per second in the pressure range of 200-250 lbs. per sq. inch gauge. The velocity should be sufficient to maintain a dense turbulent, fluidised bed 18 of catalyst and inert solid particles and gas with a zone or region 19 at the top of the bed having a temperature above the average temperature of the main bed 18. The dense fluidised bed of solid particles has a definite level L with a dilute phase suspension of solids and product vapors 20 thereabove.

A vertical conduit 22 is arranged alongside the reactor vessel 10 for receiving catalyst directly from the dense, fluidised bed 18 through connector pipe 23. An inlet 24 for the introduction of steam or other stripping gas is provided in the lower part of conduit 22 in order to displace, strip off or desorb hydrogen and/or hydrocarbons accompanying the catalyst particles withdrawn from the dense bed 18. The line 25 connecting the top of conduit 22 with the upper part of reactor 10 serves to conduct stripping gas and stripped vapors into the dilute phase in the reactor for admixture with product vapors. While the conduit or stripper 22 is shown arranged externally of the reactor vessel, it will be understood that it could also be arranged within the vessel itself, in which event the conduit would be open at the top and extend into the dilute phase 20 and one or more restriction orifices would be provided in the wall of the conduit below the dense bed level 19 to permit passage of catalyst from the dense bed into the conduit 22.

Since the catalyst and hydrocarbon feed are introduced near the bottom of reactor 10 and product vapors are removed overhead and catalyst is removed near the top of the dense catalyst bed, there is a general concurrent flow of hydrocarbon vapors and catalyst in the reactor vessel 10. It is desirable to arrange the connector 23 in the upper portion of the bed to obtain maximum concurrent flow of catalyst and oil vapors up through the bed 18 and to obtain a minimum of short-circuiting or passage of catalyst into connector 23 and conduit 22 immediately after it enters the dense bed 18. The connector 23 should be sufficiently below the maximum bed level to take care of any normal fluctuations in the depth of the dense bed. More than one connector 23 may be

provided at different levels and each connector may be provided with means to control the flow of catalyst into conduit 22. The lower end of conduit 22 is necked down and connects to conduit 27 to form therewith a standpipe for developing a fluidstatic pressure sufficient to cause the catalyst to flow through a control or slide valve 28 into transfer line 30 and thence into the regenerator 40.

The vaporous reaction products must pass through the zone 19 of higher temperature than the average temperature in bed or zone 18 whereby more refractory constituents of the reaction mixture are converted or hydroformed thereby giving better product distribution and superior properties in the final product.

The vaporous reaction products discharged overhead from the dense bed as well as the stripping gases discharged from the conduit 22 pass through a cyclone separator 31 or the like which serves to remove small amounts of catalyst that are entrained in the gaseous products. The separated catalyst particles are returned to the dense bed by the dip pipe shown and the vaporous products substantially free of catalyst are taken overhead through outlet line 32 and passed to suitable recovery or processing equipment.

The inert, heat transfer solid particles are withdrawn from the bottom of the reactor vessel through a passageway surrounding the inlet chamber 15 and pass in admixture with finely divided catalyst particles through line 33 into chamber 34. Suitable non-fluidisable packing such as Raschig rings or Berl saddles is arranged in the lower part of chamber 34 and an inlet 35 is provided at the base of the chamber for introducing steam or other inert gas for elutriating or effecting separation of finely divided catalyst particles from the inert, heat transfer solids. The finely divided catalyst particles supported in the stream of elutriating gas pass into the upper part of the chamber 34 and thence via line 36 into the upper part of reactor vessel 10. Because of the decrease in gas velocity when this stream enters the reaction vessel most of the catalyst particles drop back into the dense bed 18 while the elutriating gas mixes with the reaction product vapor and stripping gas and stripped out vapors for passage through the cyclone separators for separation of entrained catalyst particles and then to product recovery equipment.

The inert heat transfer solid particles admixed with a small amount of catalyst particles are discharged from the bottom of chamber 34 into conduit 37 which serves as a standpipe for building up a fluidstatic pressure in the heat transfer particles sufficient to cause them to flow through a slide valve

or control valve 38 into conduit 30 where they are picked up by a stream of regeneration air and conveyed into the regenerator 40.

The point of introduction of the inert heat transfer solids into the transfer line 30 occurs before the point of introduction of the main stream of spent catalyst particles. In this way, substantial amounts of inert heat transfer solids are intimately mixed with the spent catalyst particles as soon as the latter come into contact with the regeneration air. Since the rate of burning of hydrogen and carbonaceous deposits adsorbed upon the catalyst is extremely high, the inert heat transfer solid particles serve to absorb much of the heat of regeneration and thereby prevent overheating of the catalyst which would otherwise occur if the spent catalyst was passed alone with the regeneration air through the transfer line into the regenerator.

The mixture of catalyst, inert heat transfer solids and regeneration gas is discharged from transfer line 30 into inlet chamber 41 at the bottom of regenerator 40. A perforated distributor plate or grid 42 covers the top of the inlet chamber and serves to distribute the incoming mixture uniformly over the entire cross-section of the regenerator. The velocity of the gases passing through regenerator 40 is so controlled that a dense, highly turbulent fluidised bed of catalyst and inert heat transfer solids 43 having a definite level L' is formed in the regenerator. The superficial velocity of the regeneration gas through the regenerator may range from 0.3 to 1.5 feet per second depending upon the pressure. For example, at regeneration pressures of about 200-300 lbs. per sq. inch the superficial velocity should be about 1.0 ft. per second or lower.

In the event that the reforming operation in reactor 10 does not form sufficient carbon to maintain heat balance in the system, torch oil or gas may be supplied to a nozzle 44 to heat the mixture of catalyst and heat transfer solids to the desired temperature.

A vertical conduit 45 is arranged alongside the regenerator vessel 40 for receiving catalyst directly from the dense fluidised bed 43 through connector pipe 46. An inlet 47 for the introduction of air or inert stripping gas is provided in the lower part of conduit 45 in order to strip off combustion gases. Air is particularly suitable since it serves to effect a final removal of carbonaceous deposits upon the solids. It is desirable to purge the stream of stripped regenerated solid particles discharged from stripper 45 into standpipe 48 of any residual oxygen or carbon oxides by introducing a small amount of nitrogen or other inert gas through inlet line 49. Stripping and purging gases are taken overhead from stripper 130

45 and discharged through line 50 into the dilute phase in the upper part of regenerator 40. The stripped regenerated catalyst particles mixed with some inert heat transfer solids are discharged from standpipe 5 through slide valve 51 or the like into transfer line 14 where they are picked up by a stream of recycle gas and conveyed into the inlet cone or chamber 15 in the lower part 10 of the reactor.

A mixture of inert heat transfer solids and catalyst particles is withdrawn from dense bed 43 into well 52, thence through conduit 53 into elutriating chamber 54 which 15 is similar in structure and operation to the elutriating section or chamber 34 connected to the reactor vessel. Suitable non-fluidisable packing such as Raschig rings or Berl saddles is arranged in the lower part of 20 chamber 54 and an inlet 55 is provided at the base of the chamber for introducing air or inert gas for elutriating or effecting separation of finely divided catalyst particles from the inert heat transfer solids. The 25 finely divided catalyst particles supported in the stream of elutriating gas pass into the upper part of chamber 54 and thence via line 56 into the upper part of regenerator vessel 40. Because of the decrease in gas 30 velocity when this stream enters the regenerator vessel most of the catalyst particles drop back into the dense bed 43 while the elutriating gas mixes with the regeneration gases and stripping gases and passes therewith 35 through cyclone separator 64 for separation of entrained catalyst and return thereof to the dense bed 43 through dip pipe 65 and discharge via line 66 to a flue, to heat or 40 energy recovery equipment or to washing and/or storage equipment if it is desired to use this gas for stripping purposes.

Inert, heat transfer solids mixed with a small proportion of catalyst are discharged from the bottom of chamber 54 into stand- 45 pipe 57. A small amount of nitrogen or other inert stripping gas is preferably introduced into the standpipe through line 58 to purge the inert solid particle-catalyst mixture of entrained or residual oxygen or carbon oxides. The solids are discharged from 50 standpipe 57 through slide valve 59 into transfer line 60. A stream of recycle gas supplied to inlet line 61 serves to convey the hot inert solids and the small amount of 55 catalyst admixed therewith through the transfer line 60 into the upper part of the reactor for discharge against baffle 62 and addition of said solids to the top of the dense bed in the reactor.

60 The feed or charging stock to the hydroforming reactor may be a virgin naphtha, a cracked naphtha, or a Fischer-Tropsch naphtha. The feed stock is preheated alone or in admixture with recycle gas to tempera- 65 tures of from 500° to 1000°F. with the opti-

um range being about 600°-900°F. It is possible with the system shown to limit naphtha preheat to 600°F., obtainable by heat exchange with product streams and thus eliminate the necessity for a naphtha 70 preheat furnace. The recycle gas, which contains from about 50 to 70 vol. per cent. hydrogen, is preheated to temperatures of about 800°-1200°F., with temperatures below 1000°F. being preferable in order to ob- 75 viate the use of alloy tubes in the preheat furnace. The recycle gas should be circulated through the reactor at a rate of from about 1000 to 8000, preferably about 1000-3000 cu. ft. per barrel of naphtha feed. 80

The reactor system is charged with a mass of finely divided hydroforming catalyst particles. Suitable catalysts include Group VI metal oxides, such as molybdenum oxide, chromium oxide, or tungsten oxide, or mix- 85 tures thereof, upon a carrier such as activated alumina or zinc aluminate spinel. Preferred catalysts contain about 5 to 15 wt. % molybdenum oxide or from about 10 to 40 wt. % chromium oxide upon a suitable car- 90 rier. If desired minor amounts of stabilisers and promoters such as silica, calcium oxide, ceria or potassia can be included in the catalyst. The catalyst particles are, for the most part, between 300 and 400 mesh in size or 95 up to 100 microns in diameter with a major proportion between 20 and 80 microns.

The hydroforming reactor vessel should be operated at temperatures between about 850° and 925°F., preferably about 900°F. 100 and at pressures between 50 and 500 lbs. per sq. inch. Temperatures above 900°F. result in increased carbon formation and lower selectivity to gasoline fractions while at temperatures below about 900°F. operat- 105 ing severity is low and would therefore require an excessively large reaction vessel. Lowering reactor pressure below 200 lbs. per sq. inch ordinarily results in increased carbon formation which becomes excessive be- 110 low about 75 lbs. per sq. inch. Above 200 lbs., however, catalyst selectivity to light products (C_{4+}) increases rapidly. The regenerator is operated at essentially the same pressure as the reactor vessel and at tem- 115 peratures of about 1050°-1200°F.

The weight ratio of catalyst to oil introduced into the reactor should be 0.1 to 5.0. It is preferred to operate at catalyst to oil ratios of 0.3 to 1 since ratios above about 1 120 to 1.5 result in excessive carbon formation. Somewhat higher weight ratios can be used at higher pressures.

Space velocity or the weight in pounds of feed charged per hour per pound of catalyst 125 in the reactor depends upon the age or activity level of the catalyst, the character of the feed stock and the desired octane number of the product. Space velocity for a molybdenum oxide on alumina gel catalyst 130

may vary, for example, from about 1.5 wt./hr./wt. to about 0.15 wt./hr./wt.

The weight ratio of inert solids to catalyst circulated from the reactor dense bed 18 to the regenerator dense bed 43 may vary from about 1 to about 100 depending upon the relative amount of heat provided by the naphtha and recycle gas streams as compared to that supplied by the circulating inert solids. The temperature of the final reaction zone or section 19 in the reactor should be 50° to 100°F. higher, preferably about 75°F. higher than the average temperature in main reactor bed 18.

15 What we claim is:—

1. A process for hydroforming hydrocarbons boiling within the motor fuel boiling range, comprising contacting the said hydrocarbons in a reaction zone and under hydroforming conditions with a dense fluidised bed of hydroforming catalyst particles, and continuously introducing into the top of the said reaction zone a stream of hot, inert, solid particles which are maintained in a fluidised state therein, whereby the upper parts of the said reaction zone are maintained at a higher temperature than the lower parts thereof, removing spent catalyst particles from the said reaction zone and also removing the said inert solid particles from the bottom of the said reaction zone, mixing the removed inert solid particles with the removed spent catalyst particles and transferring the mixture thus obtained to a regeneration zone, wherein the spent catalyst particles are regenerated, and the inert solid particles are heated by the heat of regeneration of the catalyst particles, removing regenerated catalyst particles and recycling them to the said reaction zone, and removing hot inert solid particles and recycling them to the top of the said reaction zone.

2. A process as claimed in Claim 1 wherein the temperature of the said upper part of the reaction zone is from 50° to 100°F., preferably about 75°F., higher than the

average temperature in the main reactor bed.

3. A process as claimed in Claim 1 or Claim 2 wherein the catalyst particles have a particle diameter of up to 100 microns, 50 with a major proportion having a diameter between 20 and 80 microns.

4. A process as claimed in any of Claims 1 to 3 wherein the inert solid particles have a particle diameter not less than 100 55 microns, and preferably from 125 to 300 microns.

5. A process as claimed in any of Claims 1 to 3 wherein the inert solid particles have a bulk density of at least 1.5 times the bulk 60 density of the catalyst particles.

6. A process as claimed in any of Claims 1 to 5 wherein the said inert solid particles are metal spheres.

7. A process as claimed in any of Claims 1 to 5 wherein the said inert solid particles are ceramic balls or granules, preferably of corundum or gamma alumina or fused silica.

8. A process as claimed in any of Claims 1 to 7 wherein the said hydroforming catalyst is molybdenum oxide or chromium oxide or tungsten oxide, or mixtures thereof, on a carrier, preferably activated alumina or zinc aluminate spinel. 75

9. A process as claimed in Claim 8 wherein the catalyst is 5% to 15% of molybdenum oxide or 10% to 40% by weight of chromium oxide on the carrier.

10. A process as claimed in any of Claims 1 to 9 wherein the weight ratio of catalyst to oil in the said reaction zone is from 0.3 to 1.

11. A process as claimed in any of Claims 1 to 10 wherein the average temperature of the reaction zone is from 850° to 925°F.

13. An improved process for hydroforming hydrocarbons as herein described and illustrated in the accompanying drawing.

J. T. TYSON,

33, Davies Street, London, W.1,
Agent for the Applicants.

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1 SHEET

This drawing is a reproduction of the Original on a reduced scale.

